Group 10 Complexes

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Exploitation of a Very Strongly σ-Donating Sn^{II} Ligand: Synthesis of a Homoleptic, Octahedral Ni^{IV} Complex

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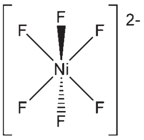
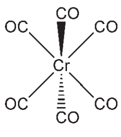
coordination modes · Group 10 elements · nickel ·
stannaborates · tin

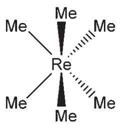
Homoleptic complexes of the transition metals have played central roles in establishing fundamental models of electronic structure and bonding. Simplifications stemming from a combination of high symmetry and a single ligand type mean that such systems have offered a valuable experimental platform on which to test theoretical models. Octahedral systems have proven to be particularly attractive in this regard, owing to the separation of (local-symmetry) metal–ligand σ- and π-bonding effects. Thus, homoleptic octahedral (or close to octahedral) systems of the types $[ML_6]^{n+}$ and $[MX_6]^{n-}$ (e.g. **I**) have, of course, given rise to much of the experimental data on which the spectrochemical and nephelauxetic series are based, and $[Cr(CO)_6]$ (**II**) is featured heavily in undergraduate textbooks outlining the origins of the 18-electron rule.[1]



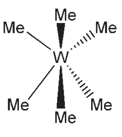
I (O_h)



II (O_h)



III (D_{3h})



IV (C_{3v})

More recently, solid-state and gas-phase structural studies of early and middle d^0 and d^1 hexamethyl complexes (e.g. **III** and **IV**) have been instrumental in establishing the extent of (and molecular-orbital rationale for) geometric distortions in such six-coordinate species that lead to reduction from O_h to D_{3h} or C_{3v} symmetry.[2] The coordination chemistry of ligands featuring the heavier Group 14 elements as donors has also generated a number of landmark results in fundamental chemistry, including multiply bonded systems and (in the context of this Highlight) complexes featuring unusually high formal metal oxidation states (for example, Pd^{VI}).[3,4] In this regard an interesting recent addition to the synthetic toolbox is a dianionic, formally Sn^{II} ligand based around a 12-atom *closo*-icosahedral cluster framework. The $[SnB_{11}H_{11}]^{2-}$ dianion was originally isolated by Todd and co-workers in 1992 as the $[Ph_3PMe]^+$ salt,[5] and it has very recently been exploited elegantly by Wesemann and co-workers in the synthesis of the homoleptic complexes $[M(SnB_{11}H_{11})_6]^{8-}$ (M = Ni (**1a**), Pd (**1b**), Pt (**1c**)), which feature octahedrally ligated M^{IV} centers.[6,7] This homologous series has provided a rare opportunity to study the bonding characteristics of a heavier Group 14 donor ligand and in particular the strong σ-donor properties which are presumably responsible (at least in part) for the isolation of such an unusually stable Ni^{IV} complex.

In the case of the palladium and platinum complexes **1b** and **1c**, the syntheses could readily be accomplished from the dipotassium salts of the corresponding hexachlorometalates and $Na_2[SnB_{11}H_{11}]$ (Scheme 1), with product isolation aided by the addition of $[Bu_3NH]Cl$ to give a highly crystalline product containing Na$^+$, K$^+$, and $[Bu_3NH]^+$ counterions in the ratio 4:2:2. In the case of the lighter congener **1a**, the lack of readily available M^{IV} precursors was neatly circumvented by the use of the Ni^{II} complex $[(\text{dpp-bian})NiBr_2]$, which by analogy with related diazabutadiene systems is thought to provide access to Ni^{IV} in situ,[8] with corresponding production of the reduced species $[(\text{dpp-bian})_2Ni]$. The salt $[Bu_3NH]_8[Ni(SnB_{11}H_{11})_6]$ was thus isolated in 64 % yield.

Complexes **1a**–**c** are remarkable not only in that they represent a complete homologous series of octahedrally ligated Group 10 complexes with the metal in the +4 oxidation state, but also in providing a robust air- and moisture-stable Ni^{IV} system. Moreover, transition-metal systems incorporating interactions with such a high number of tin (or related) donors are usually only found in Zintl ion type species featuring interstitial metal atoms.[9] The structures of the octaanionic components of **1a**–**c** were confirmed crystallographically, with the metal center lying on a center of symmetry in each case, and with Sn-M-Sn angles of 89.14(1)–90.96(1), 88.83(2)–90.08(2), and 89.09(2)–90.47(2)° for **1a**, **1b** and **1c**, respectively, thus confirming the octahedral coordination geometry. Consistent with this geometry, a relatively narrow range of M–Sn bond lengths was also measured for each of the three compounds (2.534(1)–2.548(1), 2.612(1)–2.614(1), 2.616(1)–2.619(1) Å, respectively). The Ni–Sn bond lengths measured for **1a** are significantly longer than those measured for the same stannaborate ligand in $[CpNi(PPh_3)(SnB_{11}H_{11})]^-$ (2.412(1) Å) and $[Ni(SnB_{11}H_{11})_4]^{6-}$ (2.471(1) and 2.476(1) Å; see below),[10] but are well within the sum of the

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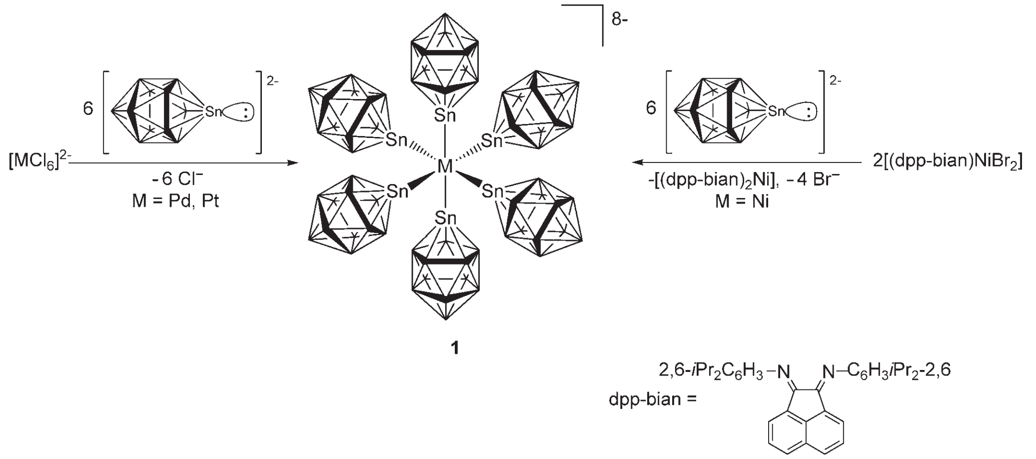

Scheme 1. Syntheses of the octahedral hexakis(stannadodecaborate) M^{IV} complexes $[M(SnB_{11}H_{11})]^{8-}$ (M = Ni (**1a**), Pd (**1b**), Pt (**1c**)).

conventional covalent radii of Ni^{II} and Sn^{II} (ca. 2.55 Å).[11] Given that each of these lower-symmetry systems features a formal Ni^{II} center (in contrast to Ni^{IV} in **1a**), the increased bond lengths for **1a** are clearly a manifestation of the high degree of steric crowding inherent in accommodating six bulky donor groups at the Ni^{IV} center (the ionic radii for Ni^{IV} and Ni^{II} are 0.48 and 0.69 Å, respectively).[11]

The NMR spectra of **1a–c** in dichloromethane or THF were measured with the aim of establishing the composition of these species in solution. The presence 1) of signals in both the $^{11}B\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR spectra, consistent with previous reports of coordinated stannaborate ligands [the $^{119}Sn\{^1H\}$ NMR spectrum shows both *cis* ($^2J = 1930$ Hz for **1a**) and *trans* ($^2J = 13490$ Hz for **1a**) two-bond couplings to ^{117}Sn], and 2) of ^{195}Pt satellites ($^1J = 7900$ Hz) in the $^{119}Sn\{^1H\}$ NMR spectrum of **1c**, together with 3) the absence of any signals for the free ligand (or of any marked broadening of the respective resonances), are taken by the authors as evidence that the six stannaborate ligands remain coordinated in solution. Consistent with this, the $^{119}Sn\{^1H\}$ NMR shift measured for nickel complex **1a** in solution ($\delta = -319$ ppm) is similar to that measured for the same compound in the solid state ($\delta = -329$ ppm). The ^{195}Pt NMR spectrum was also measured for **1c** in THF and is remarkable because of the extremely high-field chemical shift ($\delta = -7724$ ppm). Such a shift is taken as evidence for the very strongly electron-donating nature of the dianionic stannaborate ligand, a feature also evident from the low ν(Pt-H) stretching frequencies measured for related square-planar Pt^{II} hydride species, and was contextualized in terms of a greater *trans* influence than either CO or $[SnCl_3]^-$.[7a]

Further evidence for the strong σ-donor properties of $[SnB_{11}H_{11}]^{2-}$ comes from the ^{119}Sn Mössbauer spectrum of **1a** obtained at 77 K. The measured isomer shift ($\delta = 1.60\ mm\,s^{-1}$) is intermediate between those previously measured for Sn^{II} species such as $[SnB_{11}H_{11}]^{2-}$ itself and for related Sn^{IV} species such as $[MeSnB_{11}H_{11}]^-$,[5,12] thereby providing strong evidence for significant transfer of electron density from the tin center upon coordination to nickel in **1a**. While the formation of a stable Ni^{IV} species such as **1a** may itself be regarded as further evidence of such strong σ-donor properties, it is also illuminating to find that the corresponding four-coordinate Ni^{II} complex $[Ni(SnB_{11}H_{11})_4]^{6-}$ (**2a**), formed as a minor by-product (in 1% yield) during the synthesis of **1a**, adopts a square-planar geometry. The centrosymmetric structure of **2a**, determined crystallographically, features a Sn(1)-Ni-Sn(2) angle of 89.81(2)° and Ni–Sn bond lengths of 2.471(1) and 2.476(1) Å, which are significantly shorter than those measured for **1a**. A similar bond shortening (of ca. 2.5%) is observed for the analogous platinum complex, and the characterization of **2a** completes a second series of homoleptic Group 10 complexes featuring the stannaborate ligand ($[M(SnB_{11}H_{11})_4]^{6-}$, M = Ni, Pd, Pt).[7f]

In summary, the synthesis of a very stable Ni^{IV} complex and its Pd^{IV} and Pt^{IV} analogues, featuring a homoleptic octahedral hexakis-Sn^{II} donor set, has been reported. In contrast to salts of the archetypal Ni^{IV} ion $[NiF_6]^{2-}$ (**I**), which require anhydrous oxidizing conditions for their synthesis and typically generate O_2 upon hydrolysis and in some cases F_2 upon thermal decomposition,[13] complex **1a** has been effectively synthesized from a Ni^{II} precursor by a disproportionation reaction and is stable to both air and moisture. Such chemical properties provide ample evidence for the very strong σ-donor properties of the $[SnB_{11}H_{11}]^{2-}$ ligand. As with the similarly low-spin octahedral $[NiF_6]^{2-}$ dianion, classical ligand-field (Δ) and Racah (B) parameters for the stannaborate ligand will presumably be forthcoming from an in-depth analysis of the electronic spectra of $[Ni(SnB_{11}H_{11})_6]^{8-}$, provided transitions to the $^1T_{1g}$ and $^1T_{2g}$ excited states are not obscured by charge-transfer bands.[14]

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